

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 May 2003 (01.05.2003)

PCT

(10) International Publication Number
WO 03/035728 A1

(51) International Patent Classification⁷:
9/16, 9/20, C08L 25/06

C08J 9/00

(74) Agents: DE GREGORI, Antonella, et al.; Ing. Barzano' & Zanardo Milano S.p.A., Via Borgonuovo 10, I-20121 Milan (IT).

(21) International Application Number: PCT/EP02/10050

(22) International Filing Date: 3 October 2002 (03.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI01A002168 18 October 2001 (18.10.2001) IT

(71) Applicant (for all designated States except US):
POLIMERI EUROPA S.P.A. [IT/IT]; Via E. Fermi 4, I-72100 Brindisi (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): GHIDONI, Dario [IT/IT]; Via XXV Aprile 1, I-46023 Gonzaga - Mantova (IT). LANFREDI, Roberto [IT/IT]; Via Parenza 20, I-46030 Virgilio-Mantova (IT). FRIGERIO, Gilberto [IT/IT]; Via Cavour 13*, I-46010 Curtatone - Mantova (IT). CASALINI, Alessandro [IT/IT]; Viale Hermada 10, I-46100 Mantova (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/035728 A1

(54) Title: EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR THEIR PREPARATION

(57) Abstract: Expandable vinylaromatic polymers which comprise: a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0.50% by weight of a copolymerizable monomer; b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix; c) 0.05-25% by weight, calculated with respect to the polymer (a), of an inorganic filler homogeneously distributed in the polymeric matrix with a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 µm, a refraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by the Society of Dyers and Colourists, 1982), equal to or lower than 22.

EXPANDABLE VINYLAROMATIC POLYMERS AND PROCESS FOR THEIR
PREPARATION

The present invention relates to expandable vinylaromatic polymers and the process for their preparation.

More specifically, the present invention relates to a process for the preparation of expandable vinylaromatic polymers which, after expansion, have a reduced thermal conductivity also with a low density and to the products thus obtained.

Expandable vinylaromatic polymers, and among these expandable polystyrene in particular, are known products which have been used for a long time in various applicative sectors, among which one of the most important is the field of thermal insulation.

These expanded products are obtained by swelling in a closed mould beads of expanded polymer impregnated with a gas and molding the swollen particles contained inside the mould by means of the contemporaneous effect of pressure and temperature. The swelling of the particles is generally

effected with vapour, or another gas, maintained at a temperature slightly higher than the glass transition temperature (Tg) of the polymer.

A particular applicative field of expanded polystyrene 5 is that of thermal insulation in the building industry where it is generally used in the form of flat sheets. The flat expanded polystyrene sheets are usually used with a density of about 30 g/l as the thermal conductivity of the polymer shows a minimum at these values. It is not advantageous to fall below this density limit, even if it is technically possible, as it causes a drastic increase in the 10 thermal conductivity of the sheet which must be compensated by an increase in its thickness.

U.S. patent 6,130,265 describes a method for preparing 15 particles of expandable polystyrene which allows thermo-insulating sheets to be prepared for the building industry, having a density lower than 30 g/l but with a thermal conductivity analogous to that of traditional sheets. According to this method, particles of expandable polystyrene can 20 be prepared, which are capable of giving articles, for example, sheets, with a density ranging from 10 to 15 g/l and a thermal conductivity which is such as to satisfy the request of class 035 of the DIN 18164, Part 1, Standard englobing in the particle itself from 0.05 to 25% by weight 25 of graphite powder in the form of substantially spherical

particles with an average diameter ranging from 0.1 to 50 μm . More specifically, the method of the U.S. patent cited above comprises polymerizing the styrene monomer, or a solution of polystyrene in styrene, in an aqueous suspension, 5 in the presence of graphite particles and conventional reagents and/or polymerization additives. Expandable polystyrene spherical beads are thus obtained with an average diameter ranging from 0.2 to 2 mm in which the graphite in powder form is homogeneously distributed.

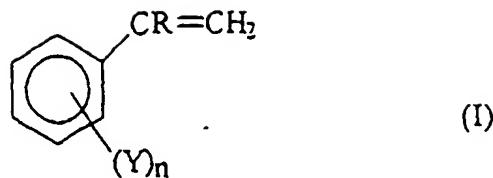
10 The Applicant has now found that it is possible to obtain expandable styrene polymers capable of providing low density expanded materials, with characteristics comparable to those of the materials obtained with the method of the known art, without having to resort to the use of an athermanous additive such as graphite which has, among other things, the defect of giving the polymer, before and after expansion, an unaesthetic grey colour, sometimes intense. It has been found, in fact, that it is possible to obtain products based on vinylaromatic polymers with a density 15 much lower than 30 g/l and with a thermal conductivity also capable of satisfying class 035 of the DIN 18164 Part 1, Standard by substituting athermanous graphite, i.e. capable of absorbing infrared radiation, with materials having a refraction index which is sufficiently higher than that of 20 the polymer and which are therefore capable of favouring 25

the reflection of infrared radiation. This result is particularly interesting as it also allows a material such as titanium dioxide to be selected, which, as it is white, does not alter the colouring of the polymer, in particular 5 polystyrene.

An object of the present invention therefore relates to expandable vinylaromatic polymers which comprise:

- a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0.50% by weight 10 of a copolymerizable monomer;
- b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix;
- c) 0.05-25% by weight, calculated with respect to the polymer 15 (a), of an inorganic filler homogeneously distributed in the polymeric matrix with a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 μm , a refraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition 20 published by The Society of Dyers and Colourists, 1982), equal to or lower than 22.

The term "vinylaromatic monomer", as used in the present description and claims, essentially refers to a product which corresponds to the following general formula:



5

wherein R is a hydrogen or a methyl group, n is zero or an integer ranging from 1 to 5 and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxy radical having from 1 to 4 carbon atoms.

10 Examples of vinylaromatic monomers having the general formula defined above are: styrene, α -methylstyrene, methylstyrene, ethylstyrene, butylstyrene, dimethylstyrene, mono-, di-, tri-, tetra- and penta-chlorostyrene, bromostyrene, methoxy-styrene, acetoxy-styrene, etc. Preferred 15 vinylaromatic monomers are styrene and α -methylstyrene.

The vinylaromatic monomers having general formula (I) can be used alone or in a mixture of up to 50% by weight with other copolymerizable monomers. Examples of these monomers are (meth)acrylic acid, C_1-C_4 alkyl esters of 20 (meth)acrylic acid, such as methyl acrylate, methylmethacrylate, ethyl acrylate, ethylmethacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of (meth)acrylic acid such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, ethylene, divinylbenzene, maleic anhydride, etc. Preferred copolymeri- 25

zable monomers are acrylonitrile and methylmethacrylate.

Any expanding agent capable of being englobed in the vinylaromatic polymeric matrix, can be used in a combination with the vinylaromatic polymers object of the present 5 invention. Typical examples are aliphatic hydrocarbons, freon, carbon dioxide, water, etc.

The inorganic filler with a refraction index higher than 1.6, preferably from 1.6 to 3, extremes included, and with a white index equal to or lower than 22, preferably 10 between 21 and 5, extremes included, can be added to the vinylaromatic polymer both by polymerization in suspension and by means of the continuous mass technique, in such quantities as to give a final concentration in the polymer ranging from 0.05-25% by weight, preferably from 0.5 to 8%. 15 The granulometry of the filler preferably ranges from 0.1 to 50 μm . The preferred inorganic filler is represented by titanium dioxide and barium sulfate.

At the end of the addition of the filler, an expandable polymer is obtained, which can be transformed to produce 20 expanded articles having a density ranging from 5 to 50 g/l, preferably from 10 to 25 g/l. These materials also have an excellent thermal insulation capacity expressed by a thermal conductivity ranging from 25 to 50 mW/mK, preferably from 30 to 45 mW/mK which is generally on an average 25 even over 10% lower than that of equivalent non-filled ex-

panded materials currently on the market, for example EXTIR A-5000 of EniChem S.p.A., as illustrated in Tables 1 and 2 enclosed. Thanks to these characteristics of the expandable polymers object of the present invention, it is possible to 5 prepare thermo-insulating articles with significant material savings or, for example, to prepare sheets having a lesser thickness than those produced with traditional non-filled polymers, with a consequent reduction in space.

Conventional additives, generally used with traditional materials, such as pigments, stabilizers, flame-retardants, antistatic agents, detaching agents, etc. can 10 be added to the expandable polymers object of the present invention.

A further object of the present invention relates to 15 the processes for the preparation of expandable polymers with an improved thermal conductivity, after expansion, with a density lower than 30 g/l.

In particular, a further object of the present invention relates to a process for preparing expandable vinylaromatic polymers which comprises polymerizing in aqueous suspension one or more vinylaromatic monomers, optionally together with at least one polymerizable comonomer in a quantity of up to 50% by weight, in the presence of an inorganic filler with a substantially spherical granulometry, 20 an average diameter ranging from 0.01 to 100 μm , a re-

fraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by The Society of Dyers and Colourists, 1982), equal to or lower than 22, and an expanding agent added before, during or after the end of the polymerization.

At the end of the polymerization, substantially spherical polymer beads are obtained, with an average diameter ranging from 0.2 to 2 mm, inside which the inorganic additive is homogeneously dispersed.

During the polymerization in suspension, polymerization additives, typically used for producing expandable vinylaromatic polymers, are adopted, such as peroxide initiators, stabilizing agents of the suspension, chain transfer agents, expanding aids, nucleating agents, plasticizers, etc. In particular, it is preferable to add flame-retardant agents during the polymerization, in a quantity ranging from 0.1% to 8% by weight, with respect to the weight of the resulting polymer. Flame-retardant agents particularly suitable for the expandable vinylaromatic polymers, object of the present invention, are brominated aliphatic, cycloaliphatic, aromatic compounds such as hexabromocyclododecane, pentabromomonochlorocyclohexane and pentabromophenyl allyl ether.

The expanding agents are preferably added during the polymerization phase and are selected from aliphatic or cy-

cloaliphatic hydrocarbons containing from 3 to 6 carbon atoms such as n-pentane, isopentane, cyclopentane or their mixtures; the halogenated derivatives of aliphatic hydrocarbons containing from 1 to 3 carbon atoms such as, for 5 example, dichlorodifluoromethane, 1,2,2-trifluoroethane, 1,1,2-trifluoroethane; carbon dioxide and water.

To improve the stability of the suspension, it is possible to use a solution of vinylaromatic polymer in the monomer, or mixture of monomers, in which the concentration 10 of polymer ranges from 1 to 30% by weight, preferably from 5 to 20%. The solution can be obtained either by dissolving a preformed polymer (for example fresh polymer or the waste products of previous polymerizations and/or expansions) in the monomer or by pre-polymerizing the monomer, or mixture 15 of monomers, in mass, in order to obtain the above concentrations, and then continuing the polymerization in aqueous suspension in the presence of the remaining additives.

Another object of the present invention relates to a process for preparing in mass and in continuous, expandable 20 vinylaromatic polymers, which comprises the following steps in series:

i. feeding a vinylaromatic polymer, as described above, to an extruder, together with an inorganic filler, having a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 μm , a refrac- 25

tion index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by The Society of Dyers and Colourists, 1982), equal to or lower than 22;

- 5 ii. heating the vinylaromatic polymer to a temperature higher than the relative melting point;
- iii. injecting the expanding agent and possible additives such as flame-retardant agents, into the molten polymer before extrusion through a die; and
- 10 iv. forming expandable beads, through a die, in a substantially spherical form with an average diameter ranging from 0.2 to 2 mm.

A detailed method for preparing vinylaromatic polymers in mass and in continuous is provided in European patent EP 15 126,459.

At the end of the polymerization, either it be carried out in suspension or in continuous mass, the expandable beads produced are subjected to pre-treatment generally applied to conventional expandable beads and which essentially consists in:

1. coating the beads with a liquid antistatic agent such as amines, tertiary ethoxylated alkylamines, ethylene oxide-propylene oxide copolymers, etc. The purpose of this agent is to facilitate both the adhesion of the 25 "coating" and also the screening of the beads prepared

in suspension;

2. applying the "coating" to the above beads, said coating essentially consisting of a mixture of mono-, di- and tri-esters of glycerin (or other alcohols) with fatty acids and of metallic stearates such as zinc and/or magnesium stearate.

5 Alternatively, the inorganic filler can also be added in the coating, together with the mixture of esters.

Some 10 illustrative but non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

EXAMPLE 1

A mixture of 150 parts by weight of water, 0.1 parts of sodium pyrophosphate, 100 parts of styrene, 0.15 parts 15 of benzoyl peroxide, 0.25 parts of ter-butyl perbenzoate and 1 part of titanium dioxide with a substantially spherical granulometry and an average diameter of about 0.2 μm , are charged into a closed, stirred container. The mixture is heated to 90°C under stirring.

20 After about 2 hours at 90°C, 4 parts of a solution at 10% of polyvinylpyrrolidone are added. The mixture is heated, under stirring, for a further 2 hours to 100°C, 7 parts of a 70/30 mixture of n-pentane and i-pentane are added and the mixture heated for a further 4 hours to 25 125°C.

The beads of expandable polymer thus produced are subsequently recovered, washed with deionized water, dried in a stream of warm air, added with 0.02% of ethoxylated amine, and screened by separating the fraction with a diameter ranging from 1 to 1.5 mm.

5 0.2% of glycerylmonostearate and 0.05% of magnesium stearate are then added to the fraction.

The product is pre-expanded with vapour at a temperature of 100°C for three contact times and aged for a day

10 (density in Table 1).

A part of the beads is expanded a second time to reach even lower densities.

Both the beads expanded once only and those expanded twice were used for the moulding of blocks (dimensions 1040

15 x 1030 x 550 mm) at a pressure of 0.4 bars, and the cooling time was measured (data in Table 2 - sheet 1).

The blocks were then evaluated (shrinkage, or the difference between the volume of the block and the volume of the mould), and cut to prepare flat sheets for measuring the

20 sintering and thermal conductivity. The thermal conductivity was 36.7 mW/mK whereas that of a sheet having the same density prepared with a traditional non-filled reference product (EXTIR A-5000), was 42.5 mW/mK.

Table 2 indicates the physical characteristics of an

25 expanded polystyrene block obtained with the expandable

beads, object of the present invention, in a first and second expansion and compared with an analogous block obtained from the commercial reference product. The block obtained with the beads object of the present invention surprisingly 5 shows a drastic increase in the sintering degree.

EXAMPLE 2

A polystyrene having a Melt Index of 10 g/10' at 200°C/5 kg premixed with titanium dioxide alone (2 and 4%) in a first phase, and with barium sulfate alone (2%) in a 10 second phase, is fed into a twin-screw extruder equipped with a feeding hopper. After bringing the polymer to the molten state, 6 parts of a mixture of n-pentane/i-pentane with a weight ratio of 70/30, are injected.

The resulting mass is drawn through an extrusion head 15 equipped with holes. The polymer emerging from the holes is cut by a series of rotating knives in contact with the surface of the die in order to obtain substantially spherical beads having an average diameter of about 1.2 mm. The die is immersed in a water bath.

20 The beads are sent by the stream of water, cooled to 35°C, separated from the water and dried in a stream of warm air.

Ethoxylated amine and the coating are then added to the beads as described in Example 1.

25 The expansion and moulding were effected as described

in Example 1. The thermal conductivity was about 36 and 35.5 mW/mK with 2 and 4% respectively of titanium dioxide.

The thermal conductivity value of 36.7 mW/mK was obtained, on the other hand with a flat sheet containing 2% 5 by weight of BaSO₄, with a density however of 17 g/l.

Table 2 indicates the physical characteristics of expanded blocks obtained from expandable beads modified with titanium dioxide. Also in these cases, the blocks obtained with the beads, object of the present invention, show a 10 drastic increase in the sintering degree with respect to the reference block.

TABLE 1

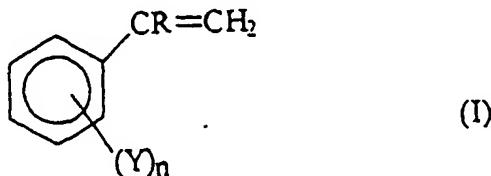
| Reference | <u>Contact time</u> (min.) | Density (g/l) |
|----------------------------------|-------------------------------|------------------------------|
| | 1 | 20.5 |
| | 2 | 17.2 |
| | 3 | 15.5 |
| Example 1 (1% TiO ₂) | | |
| | 1 | 19.5 |
| | 2 | 15.6 |
| | 3 | 14.2 |
| 20 | | |
| Sheets | DENSITY | THERMAL CONDUCTIVITY (mW/mK) |
| Reference | 14 g/l | 42.5 |
| Sheet 1 (1% TiO ₂) | 14 g/l | 36.7 |
| Sheet 2 (2% TiO ₂) | 14 g/l | 36 |
| Sheet 3 (4% TiO ₂) | 14.4 g/l | 35.5 |

TABLE 2 - Blocks from beads of first and second expansion

| Reference | | |
|--------------------------------|------|--------|
| Density (g/l) | 16.5 | 7.8 |
| Cooling time | 30' | 2' 30" |
| Shrinkage (mm) | -7 | -5 |
| Sintering (%) | 15 | 20 |
| | | |
| Sheet 1 (1% TiO ₂) | | |
| Density (g/l) | 15 | 8.3 |
| Cooling time | 25' | 2' 30" |
| Shrinkage (mm) | -2 | -3 |
| Sintering (%) | 85 | 35 |
| | | |
| Sheet 2 (2% TiO ₂) | | |
| Density (g/l) | 18.1 | 8 |
| Cooling time | 30' | 2' |
| Shrinkage (mm) | -4 | -4 |
| Sintering (%) | 80 | 30 |
| | | |
| Sheet 3 (4% TiO ₂) | | |
| Density (g/l) | 15 | 8.4 |
| Cooling time | 25' | 2' 30" |
| Shrinkage (mm) | -2 | -4 |
| Sintering (%) | 80 | 40 |

CLAIMS

1. Expandable vinylaromatic polymers which comprise:
 - a) a matrix obtained by polymerizing 50-100% by weight of one or more vinylaromatic monomers and 0.50% by weight of a copolymerizable monomer;
 - b) 1-10% by weight, calculated with respect to the polymer (a), of an expanding agent englobed in the polymeric matrix;
 - c) 0.05-25% by weight, calculated with respect to the polymer (a), of an inorganic filler homogeneously distributed in the polymeric matrix with a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 μm , a refraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by The Society of Dyers and Colourists, 1982), equal to or lower than 22.
2. The polymers according to claim 1, wherein the vinylaromatic monomer is selected from those corresponding to the following general formula:



wherein R is a hydrogen or a methyl group, n is zero or an integer ranging from 1 to 5 and Y is a halogen, such as chlorine or bromine, or an alkyl or alkoxy

radical having from 1 to 4 carbon atoms.

3. The polymers according to claim 1 or 2, wherein the vinylaromatic monomers having general formula (I) are used in a mixture, of up to 50% by weight, with other copolymerizable monomers selected from (meth)acrylic acid, C₁-C₄ alkyl esters of (meth)acrylic acid, amides and nitriles of (meth)acrylic acid, butadiene, ethylene, divinylbenzene, maleic anhydride.

4. The polymers according to claim 3, wherein the copolymerizable monomers are acrylonitrile and methylmethacrylate.

5. The polymers according to any of the previous claims, wherein the inorganic filler has a refraction index ranging from 1.6 to 3 and a white index ranging from 21 to 5, extremes included.

6. The polymers according to any of the previous claims, wherein the inorganic filler is present in concentrations ranging from 0.5 to 8% by weight and with a granulometry ranging from 0.1 to 50 μm .

7. The polymers according to any of the previous claims, wherein the inorganic filler is titanium dioxide or barium sulfate.

8. Expanded articles obtained with the expandable vinylaromatic polymers according to any of the previous claims, having a density ranging from 5 to 50 g/l and

a thermal conductivity ranging from 25 to 50 mW/mK, generally even over 10% lower with respect to that of equivalent non-filled expanded materials.

9. A process for preparing expandable vinylaromatic polymers which comprises polymerizing in aqueous suspension one or more vinylaromatic monomers, optionally together with at least one polymerizable comonomer in a quantity of up to 50% by weight, in the presence of an inorganic filler with a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 μm , a refraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by The Society of Dyers and Colourists, 1982), equal to or lower than 22, and an expanding agent added before, during or after the end of the polymerization.
10. The process according to claim 9, wherein, at the end of the polymerization, substantially spherical beads of polymer are obtained, with an average diameter ranging from 0.2 to 2 mm inside which the inorganic additive is homogeneously dispersed.
11. The process according to claim 9 or 10, wherein during the polymerization flame-retardant agents are added in a quantity ranging from 0.1 to 8% by weight, with respect to the weight of the resulting polymer.

12. The process according to claim 11, wherein the flame-retardant agents are brominated aliphatic, cycloaliphatic, aromatic compounds.
13. The process according to any of the claims from 9 to 5 12, wherein the expanding agents are added during the polymerization phase and are selected from aliphatic or cycloaliphatic hydrocarbons containing from 3 to 6 carbon atoms; halogenated derivatives of aliphatic hydrocarbons containing from 1 to 3 carbon atoms; carbon dioxide and water.
14. The process according to any of the claims from 9 to 13, wherein the polymerization in suspension takes place through a solution of vinylaromatic polymer in the monomer, or mixture of monomers, wherein the concentration of polymer ranges from 1 to 30% by weight.
15. A process for preparing in mass and in continuous, expandable vinylaromatic polymers, which comprises the following steps in series:
 - i. feeding a vinylaromatic polymer, as described 20 above, to an extruder, together with an inorganic filler, having a substantially spherical granulometry, an average diameter ranging from 0.01 to 100 μm , a refraction index higher than 1.6 and a white index, as defined in "Colour Index" (third edition published by The Society of Dyers and

Colourists, 1982), equal to or lower than 22;

- ii. heating the vinylaromatic polymer to a temperature higher than the relative melting point;
- iii. injecting the expanding agent and possible additives, into the molten polymer, before extrusion through a die; and

(iv) forming beads, optionally expandable, through a die, in a substantially spherical form with an average diameter ranging from 0.2 to 2 mm.

10 16. The process according to any of the previous claims from 9 to 15, wherein the expandable beads produced are pretreated by means of methods generally applied to beads produced with conventional processes and which essentially consist in:

15 a) coating the beads with a liquid antistatic agent such as amines, tertiary ethoxylated alkylamines, ethylene oxide-propylene oxide copolymers;

b) applying the coating to the beads thus treated, said coating essentially consisting of a mixture of

20 mono-, di- and tri-esters of glycerin with fatty acids and of metallic stearates such as zinc and magnesium stearate.

17. The process according to any of the claims from 9 to 15, wherein the inorganic filler is also added in the coating together with the mixture of esters.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/10050A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/00 C08J9/16 C08J9/20 //C08L25/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | PATENT ABSTRACTS OF JAPAN vol. 2000, no. 04, 31 August 2000 (2000-08-31) & JP 2000 017096 A (ACHILLES CORP), 18 January 2000 (2000-01-18) abstract ---- | 1-17 |
| A | PATENT ABSTRACTS OF JAPAN vol. 2000, no. 01, 31 January 2000 (2000-01-31) & JP 11 279319 A (ACHILLES CORP), 12 October 1999 (1999-10-12) abstract ---- | 1-17 |
| | | |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

24 December 2002

07/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Oudot, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/10050

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|-------------------------|------------------|
| JP 2000017096 A | 18-01-2000 | NONE | |
| JP 11279319 6 A | | NONE | |

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.